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Experimental Determination of the Heat of Dissociation of $N_2O_4 \rightarrow 2NO_2$ from the Temperature Dependence of Absolute Infrared Intensities*

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The heat of dissociation of N_2O_4 has been determined from measurements of the temperature dependence of the integrated absorption of NO_2 and N_2O_4 vibration-rotation bands. Results have been obtained that are in acceptable accord with the earlier estimate of Giauque and Kemp.

ABSOLUTE infrared intensity measurements have been performed by using the technique of self-broadening[1] on a number of vibration-rotation bands belonging to NO_2 and N_2O_4. A complete account of the experimental results is given elsewhere[2]; the experimental data were obtained on the equilibrium gases formed over liquid N_2O_4.

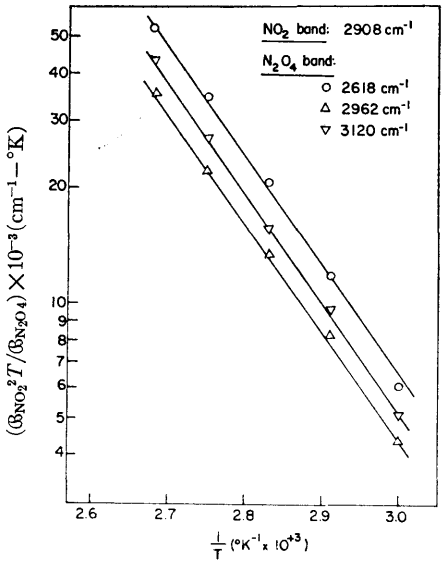

FIG. 1. Plots for determining ΔH^0 for the reaction $N_2O_4 \rightarrow 2NO_2$ from experimental values of the parameters $\mathcal{B}$. The three curves were obtained using the strongest N_2O_4 bands in the region from 1 to 5 microns (NO_2 band: 2908 cm^{-1}; N_2O_4 bands: ○ 2618 cm^{-1}; △ 2962 cm^{-1}; ▽ 3120 cm^{-1}).

The measured temperature dependence of the integrated intensities may be used to determine the heat of dissociation. Using standard procedures, we define the quantity

$$\mathcal{B}=\int_{\omega_1}^{\omega_2}\left[\ln\frac{I_\omega^{o,a}}{I_\omega^{a}}\right]d\omega, \qquad (1)$$

where $I_\omega^{o,a}$ and I_ω^{a} denote, respectively, the incident and transmitted apparent flux densities at the wave number ω. The integration limits in Eq. (1) are chosen in such a way that an entire vibration-rotation band is included between ω_1 and ω_2. It is well known that, if the spectral absorption coefficient is constant over the wave number range corresponding to the effective slit width, then

$$d\mathcal{B}/dX=\alpha, \qquad (2)$$

where $X=pl$ is the optical depth in cm-atm if p is the partial pressure of absorber in atm and l denotes the geometric length in cm; α represents the integrated intensity of the vibration-rotation band in cm^{-2}-atm^{-1} at the temperature at which the experiment was performed.

If we consider two bands, one belonging to NO_2 and another belonging to N_2O_4, then it is apparent from Eq. (2) that

$$p_{NO_2}=\mathcal{B}_{NO_2}/\alpha_{NO_2}l$$

and

$$p_{N_2O_4}=\mathcal{B}_{N_2O_4}/\alpha_{N_2O_4}l,$$

provided adequate broadening of the spectral lines has been achieved. For the small temperature range covered in the experimental studies and extending from about 295°K to about 395°K,[3] we may assume, in good approximation, that the integrated intensities are inversely proportional to the absolute temperatures T. Hence

$$\alpha_{NO_2}=\alpha_{o,NO_2}(T_o/T)$$

and

$$\alpha_{N_2O_4}=\alpha_{o,N_2O_4}(T_o/T),$$

where the subscript o identifies suitable reference conditions. The preceding expressions lead to the following relation for the equilibrium constant at constant pressure:

$$K_p\equiv\frac{p_{NO_2}^2}{p_{N_2O_4}}=\left(\frac{\alpha_{o,N_2O_4}}{\alpha_{o,NO_2}^2T_ol}\right)\left(\frac{\mathcal{B}_{NO_2}^2T}{\mathcal{B}_{N_2O_4}}\right). \qquad (3)$$

For specified reference conditions and constant geometric length l, the first factor in Eq. (3) is independent

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[1] S. S. Penner and D. Weber, J. Chem. Phys. **19**, 817 (1951).

[2] A. Guttman, Ph.D. thesis, California Institute of Technology, Pasadena, 1962.

[3] The corresponding equilibrium vapor pressures of NO_2 over liquid N_2O_4 lie between about 1.5 and 25.0 atm; see H. H. Reamer and B. H. Sage, Ind. Eng. Chem. **44**, 185 (1952).

of temperature. Hence it follows from Eq. (3) that

$$\frac{d \ln K_p}{d(1/T)} = -\frac{\Delta H^\circ}{R} = \frac{d \ln(\mathfrak{B}_{NO_2}{}^2 T/\mathfrak{B}_{N_2O_4})}{d(1/T)}, \quad (4)$$

where ΔH° is the molar heat of dissociation of N_2O_4 and R represents the molar gas constant.

Experimentally determined values of the quantity $\mathfrak{B}_{NO_2}{}^2 T/\mathfrak{B}_{N_2O_4}$ for the NO_2 band centered at 2908 cm^{-1} and for three N_2O_4 bands (centered at 2618, 2962, and 3120 cm^{-1}) are plotted in Fig. 1 as a function of $1/T$. The geometric length l was set at 0.124 cm by using a suitable spacer.[2] The data shown in Fig. 1 yield values of $\Delta H^\circ = 13\,070$, 12 980, and 13 160 cal/mole of N_2O_4 for the curves corresponding to the 2618, 2962, and 3120 cm^{-1} bands of N_2O_4, respectively. These results are in reasonably satisfactory agreement with the value $\Delta H^\circ = 13\,693 \pm 14$ cal/(mole of N_2O_4) reported by Giauque and Kemp[4] at 298°K.

The preceding results provide an important check on the self-consistency of the absolute intensity measurements although they have no direct bearing on the absolute accuracy of the results. The procedure for determining heats of reaction by measuring the temperature dependence of (absolute) infrared intensities is clearly applicable also to other molecules. An experiment similar to that described in the present note was suggested to one of us (S.S.P.) by Professor Farrington Daniels in 1942.

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[4] W. F. Giauque and J. D. Kemp, J. Chem. Phys. **6**, 40 (1938). It is easily shown that the equation of state proposed by Giauque and Kemp leads to cancellation of real gas effects in the expression for the equilibrium constant.